

Fractional Crystallization Calculations based on
Whole-rock and Phenocryst Element Oxide Weight Percentages
from Agina, Aegean Sea, Greece

by
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ABSTRACT

Fractional crystallization calculations were performed on four representative lava samples from Aegina. The entire SiO_2 range found in the calc-alkaline suite on Aegina was used, basaltic-andesite to dacite. The calculations were performed using ten element oxide weight percents from XRF whole-rock data and microprobe phenocryst data obtained previously to determine whether the evolved magmas could have been generated from the more primary magmas via fractional crystallization.

The results of the calculations showed that fractional crystallization must have occurred throughout the lava sequence on Aegina, but K_2O and TiO_2 contents are inconsistent with the operation of fractionation alone during the early stages of magma evolution. Thus assimilation accompanied fractional crystallization in the lower crust and fractional crystallization occurred as the primary differentiation mechanism in the upper crust.

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I. INTRODUCTION

Aegina lava samples exhibit a wide range of chemical compositions, ranging from basaltic-andesite to dacite, which has been assumed to reflect magma evolution via fractional crystallization. Fractional crystallization calculations, from oxide weight percents of whole-rock and phenocryst mineral-elements, were performed to determine if the magma differentiation occurred by fractional crystallization alone. According to published Sr-isotope data (1), assimilation could have also accompanied fractional crystallization during the early, basaltic-andesite stage of magma evolution.

Four representative lava samples were chosen from Aegina which encompass the total range of SiO_2 content present. The samples were studied petrologically to determine the minerals present, textures, and degree of chemical alteration for each sample. XRF analyses were performed on these samples to determine the whole-rock major element oxide percent and then electron microprobe analyses were done to acquire the individual phenocryst element oxide percent. These data were then recalculated to 100 percent and least-squares mixing calculations were performed to determine if fractional crystallization could alone explain the observed chemical variation.

Aegina lavas were selected for the following reasons:

(1) Stratigraphic field relations had been established from previous workers (Barton, personal communication, 1986).

(2) Lava samples demonstrated a wide range of chemical compositions, so that the evolutionary history could be traced in detail.

(3) Lava samples are relatively young and are fresh.

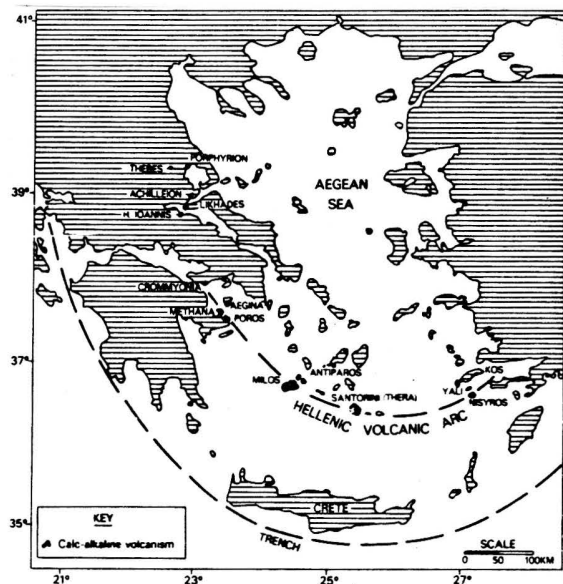
(4) The unique setting allowed insight into the evolution of

calc-alkaline magma evolution from an intracrustal storage chamber.

(5) Previous studies indicated fractional crystallization was an important factor in the magma evolution on Aegina, and also Sr-isotope data showed that assimilation possibly accompanied fractional crystallization during the early stages of magma evolution.

II. GEOLOGIC SETTING

The Hellenic arc, located in the southern section of the Aegean sea (Fig. 1), extends from the Greek mainland in the west to the Turkish mainland in the east. A double arc structure has been proposed for this region (3), and the volcanic activity is thought to be related to subduction of the African plate beneath the Aegean microplate (4,5), beginning around 12 my B.P. (3). The volcanic center of Aegina, located in the northwest of the arc, is a member of the outer arc and activity began around 3 my B.P. (3), compared to the volcanic centers in the central region, which began around 1.6-0.2 my B.P. Gravity and seismic studies



suggest crustal thickness beneath Aegina is about 40 km compared to the central region which is less than 20 km (Barton, personal communication, 1986). Heat flow is relatively high, and probably reflects upwelling of mantle material along the central portion of the arc.

Submarine trenches are located

Figure 1. The Hellenic arc. south of Crete, but no oceanic crust has been found as of yet. This region, therefore, is unique in that calc-alkaline volcanism is associated with continental-continental collision. Aegina lavas provide an excellent test of the fractional crystallization hypothesis, since they show a wide range of compositions, are fresh and unaltered, and have evolved within the continental crust which provides the opportunity for assimilation to occur.

III. ANALYTICAL TECHNIQUES

The petrographic analyses of the four representative thin sections from Aegina lavas were done on a polarizing light microscope at The Ohio State University. Automated XRF analyses on the same samples were done at The State University of Utrecht by M. Barton, and the electron microprobe analyses were also completed at Utrecht (Netherlands) by M. Barton. The recalculation of XRF and microprobe data to 100 percent was done manually and then least-squares mixing calculations were performed with these data to test whether or not the lavas evolved via fractional crystallization alone. The computer calculations were done on the main computer at The Ohio State University.

IV. RESULTS

Petrographic analyses

Each sample was studied through the polarizing light microscope and the respective compositions and textures were recorded. All the samples exhibited a holocrystalline texture, but the more acidic samples were slightly hypocrystalline. The primary phenocryst phases included: olivine, plagioclase, pyroxene (Cpx and Opx), hornblende, biotite, and opaques. Resorption is common in phenocrysts as is a poikiloblastic texture.

The phenocrysts are set in a fine-grained, intersertal to intergranular groundmass with an amygdaloidal texture occasionally present. Dacites are more trachytic, but flow patterns are generally absent in the more mafic samples.

Basaltic-andesite. The phenocryst phases present include: olivine, plagioclase, pyroxene, and opaques. The olivine, forsterite, is found in small, euhedral to subhedral phenocrysts with alteration and resorption present along the edges of the crystals. The plagioclase phenocrysts, andesine to labradorite, are large, anhedral grains exhibiting resorption and reaction textures. Embayment and oscillatory zoning are also common. Clinopyroxene, augite, is subhedral, sector zoned, and commonly resorbed. The augite crystals sometimes appear as glomerophors and contain inclusions of opaques. The opaques are euhedral to anhedral in shape and occur as inclusions in the larger phenocrysts and in the groundmass.

The groundmass consists mainly of plagioclase microlites, but clinopyroxene and opaques are also present.

Andesite. The phenocryst phases present include: olivine, plagioclase, pyroxene, biotite, hornblende, and opaques. The olivine, forsterite, is present in two crystal sizes. The larger

grains show substantial alteration in comparison to the smaller grains. Clinopyroxene, augite, is frequently twinned and sector zoned and is usually highly altered. Glomeroporphyritic intergrowths with plagioclase and opaques are also common. The plagioclase, andesine to labradorite, commonly displays oscillatory zoning. Many plagioclase crystals are resorbed and contain inclusions of opaques. The hornblende crystals are anhedral and rimmed by opaques. Alteration is common as are inclusions of alkali-feldspars. The biotite is substantially altered and appears almost in an opaque phase. Opaques are generally cubic euhedral in shape and are found as either individual crystals or as inclusions in plagioclase, olivine, and pyroxene phenocrysts.

The groundmass contains microlites of plagioclase, pyroxene, and opaques, and it exhibits semi-amygdaloidal and trachytic textures.

Dacite. Phenocrysts of feldspars, pyroxene, hornblende, and opaques are present. The plagioclase is less calcic in composition than andesine and exhibits oscillatory zoning. The crystals are generally subhedral and contain inclusions of opaques. The clinopyroxene, augite, is concentrically zoned and the crystals are anhedral to subhedral in shape. Inclusions of opaques are frequently found in the grains. Olivine, fayalite, is present in small amounts as are hornblende and alkali-feldspar. These three minerals are subhedral and anhedral in shape. The opaques occur as cubic euhedral microphenocrysts. All of the above mentioned minerals occur in glomeroporphyritic aggregates.

The groundmass contains plagioclase microlites, opaques, pyroxene, and glass. This groundmass exhibits a trachytic texture.

Several of the mineral phases show a systematic trend within the observed compositional range for Aegina (basaltic-andesite to

dacite). The plagioclase becomes more albitic, the pyroxene exhibits a Ca-depletion, and the olivine becomes Fe-rich. These compositional trends correspond to the expected fractionation trends within a calc-alkaline sequence.

XRF analyses

XRF analyses were completed for each of the four representative samples. The whole-rock mineral-element percentages were determined for ten oxides and the results were recorded in Table I. These oxide weight percents were then used in the fractional crystallization calculations.

Table I: Whole-rock mineral-element percents for ten oxides in each Aegina sample.

<u>OXIDES</u>	<u>AEG 3</u>	<u>AEG 14</u>	<u>AEG 13</u>	<u>AEG 17</u>
SiO ₂	55.25	57.69	60.93	69.39
TiO ₂	0.76	0.61	0.51	0.30
Al ₂ O ₃	17.41	17.29	16.57	15.62
FeO	6.97	5.87	5.23	2.40
MnO	0.16	0.16	0.14	0.09
MgO	4.49	4.84	3.82	1.24
CaO	8.99	8.32	7.40	3.76
Na ₂ O	3.34	3.21	3.14	3.67
K ₂ O	1.72	1.99	2.23	3.52
P ₂ O ₅	0.00	0.00	0.00	0.00

Microprobe analyses

The electron microprobe analyses done on these four samples provided the mineral-element oxide weight percents for the olivine, plagioclase, pyroxene (Cpx), and opaque phenocrysts present. Energy dispersive techniques were used so that the elements in each mineral were determined simultaneously, thus avoiding problems with machine calibration. Again, the same ten oxides were

calculated. The fractional crystallization calculations, however, only required phenocryst element oxide data from the three most mafic samples. The most suitable compositions of each phenocryst phase present in each sample was selected and the data were recalculated to 100 percent. Principally, the phenocryst phases to be used were chosen in the following manner:

- 1) The olivine that contained the most MgO.
- 2) The plagioclase that contained the most CaO, but the least Na₂O.
- 3) The pyroxene that contained the most MgO, but the least amount of TiO₂ and Al₂O₃.
- 4) The opaque that contained the least amount of TiO₂ and Al₂O₃.

The fractional crystallization calculations were then performed using the data from Table II.

Fractional crystallization calculations

Fractional crystallization calculations were performed on these four samples by least-squares mixing methods to determine if the evolved magmas could be generated from the more primitive magmas observed on Aegina. The mixing calculations used the whole-rock and phenocryst oxide percents from the lower SiO₂ sample together with the whole-rock oxide percent of the next highest SiO₂ sample to perform each subsequent fractionation calculation. There were a total of three calculations, one for each evolved magma composition.

The difference between observed and calculated magma compositions (residuals) were compared with analytical error, and a result was considered satisfactory only if all residuals were smaller than analytical errors for the particular oxide. This approach differs from that of previous workers who have accepted results

Table II: Phenocryst element oxide weight percents used for the fractional crystallization calculations.

	AEGINA 3				AEGINA 14				AEGINA 13			
	<u>Oliv</u>	<u>Cpx</u>	<u>Plag</u>	<u>Opaq</u>	<u>Oliv</u>	<u>Cpx</u>	<u>Plag</u>	<u>Opaq</u>	<u>Oliv</u>	<u>Cpx</u>	<u>Plag</u>	<u>Opaq</u>
SiO ₂	39.74	53.03	47.78	0.00	41.24	52.73	49.88	0.00	40.27	53.34	51.87	0.00
TiO ₂	0.00	0.19	0.00	11.19	0.00	0.31	0.00	4.77	0.00	0.14	0.00	5.78
Al ₂ O ₃	0.00	2.22	32.64	2.39	0.27	2.49	31.22	1.63	0.00	0.46	29.98	2.03
FeO	16.20	6.04	0.83	82.90	11.39	6.56	0.65	91.50	13.95	3.52	1.22	83.35
MnO	0.18	0.12	0.00	0.48	0.00	0.29	0.00	0.51	0.21	0.00	0.00	0.53
MgO	43.68	16.52	0.34	2.53	46.53	17.33	0.00	1.14	46.90	18.42	0.77	0.35
CaO	0.18	21.72	16.26	0.24	0.27	19.58	15.19	0.08	0.16	21.56	13.81	0.12
Na ₂ O	0.00	0.00	2.08	0.00	0.00	0.51	2.87	0.00	0.00	0.00	3.37	0.00
K ₂ O	0.00	0.00	0.05	0.00	0.00	0.10	0.15	0.00	0.00	0.00	0.15	0.00
P ₂ O ₅	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

for which the total sum of the residuals squared (SSR) is less than 1.5. The sum of the residuals squared for each of the three fractionation calculations was less than one, and almost every oxide weight percent (except K_2O and TiO_2) was within analytical error.

Failure by the calculations to reproduce the K_2O content to within analytical error suggests that a greater than normal amount of K was concentrated in the residual melt than could be explained by fractional crystallization alone. Generally, K is incompatible in early forming minerals so the residual melt becomes enriched with respect to K. Since the concentration of K should increase as a result of fractional crystallization and assimilation (1), and this problem was more apparent during the basaltic-andesite to andesite fractionation stage than in the other stages, assimilation could have possibly occurred simultaneously with fractional crystallization.

Assimilation occurs more readily deeper in the crust where higher temperatures are found, because crustal rocks are hotter and the ascending magma will expend less energy heating the crustal rocks to their fusion temperature than if the crustal rocks were cool. The incorporation of additional K from the melting crustal rocks would increase the amount of K in the residual melt.

Since TiO_2 contents cannot be reproduced to analytical error, they must have been too low in the predicted compositions, otherwise a higher Ti opaque should have been used in the fractional crystallization calculations.

Hence, the concentrations of K and Ti in the lavas cannot be modeled using least-squares techniques, since this approach presupposes that fractional crystallization is the only evolutionary mechanism.

V. DISCUSSION

Fractional crystallization depends upon non-reaction or incomplete reaction of a magma with its crystalline products, and will result in a wide range of lava compositions with time. Since certain elements partition strongly into the various phases (solid and liquid) the magmas will change composition regularly, depending upon 1) the nature and composition of the phases, and 2) the proportions of crystalline phases to melt. If crystals are completely or partially prevented from reacting with the changing liquid composition, strong melt fractionation occurs and the final melt will be different from that produced through equilibrium crystallization (2).

The calc-alkaline lava suite from Aegina exhibits this type of changing compositional sequence. During fractional crystallization of the magmas, the Mg and Al-rich mafic magmas crystallize first leaving the more acidic Na-rich magmas to crystallize last. The petrologic and major element studies confirm this fractionation trend in lava compositions.

The fractional crystallization calculations confirm that removal of the observed phenocryst phases could generate many of the actual compositional trends for the evolved Aegina lavas. The results also show that the inability of the calculations to reproduce K and Ti concentrations to within analytical error (especially during the basaltic-andesite to andesite stage) could signify simultaneous assimilation and fractional crystallization during the early magma evolution. This result is consistent with the results of previous studies (1). An increase in the incompatible element, K, with increasing SiO_2 content shows that the volcanic magmas of Aegina are related through fractional crystallization, but that assimilation played a role in the early stages of magma differentiation.

Sr-isotope ratios for Aegina range from 0.7041-0.7068 (3), and thus fall between values appropriate for the upper mantle and average continental crust. They provide conclusive evidence that assimilation occurred. (Sr ratios do not fractionate relative to each other during fractional crystallization). Sr ratios in the Hellenic arc tend to increase in a northwesterly direction toward Aegina, correlating with the increasing crustal thickness and opportunity for assimilation(1). Note that it is extremely unlikely a mantle-derived magma will traverse a significant thickness of crust without some interaction occurring.

Assimilation occurs more readily in the deeper crust where the ambient temperatures are higher, causing crustal rock to melt with input of a relatively small amount of energy. Since K is incompatible, it preferentially enters the residual melt causing an anomalous increase in the concentration of the element compared with that expected to result from fractional crystallization alone. Combined fractional crystallization and assimilation during the initial magma evolution stages would account for the failure of the least-squares modeling to account for K concentrations. The high and variable Sr ratios found in the Aegina lavas are consistent with the effects of crustal contamination also.

VI. CONCLUSION

Through the data acquired from petrographic studies, previous work, and fractional crystallization calculations, magma differentiation is shown to have occurred largely via fractional crystallization on Aegina. The main lines of evidence are:

1) The compositional range of calc-alkaline lavas on Aegina, from basaltic-andesite to dacite.

2) The results from the fractional crystallization calculations show that generation of the evolved magma from the more primary magma can occur via removal of the observed phenocryst phases.

Fractional crystallization and assimilation are thought to have occurred simultaneously during the earlier, more mafic, episode of magma evolution. This crustal contamination of the primary magma during the ascent through the lower crust is deduced from:

1) The inability to predict K_2O and TiO_2 oxides to within analytical error in the initial stages of evolution, being the least fractionated part of the sequence. These two oxides, however, do correlate better in the evolved lavas.

2) The tendency for the Sr ratios to fall between those appropriate for the upper mantle and average continental crustal values.

Hence, the most primitive lavas have experienced combined fractionation and assimilation, presumably in the lower crust, whereas the more evolved lavas (andesite to dacite) evolved via fractional crystallization in shallow chambers from the contaminated parental magmas.

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